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**FIRST QUARTERLY REPORT**

on

**THE INVESTIGATION OF NEW  
ELECTROCHEMICAL SYSTEMS**

to

**SQUIER SIGNAL LABORATORIES, SCEL  
POWER SOURCES BRANCH**

**Period of Report  
March 1, 1953, to June 1, 1953**

**Contract No. DA-36-039-SC-42682  
Department of the Army Project No. 3-99-09-022  
Signal Corps Project No. 162B**

**BATTELLE MEMORIAL INSTITUTE  
505 King Avenue  
Columbus 1, Ohio**

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by

**L. D. McGraw, A. B. Tripler, Jr., and C. L. Faust**

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**BATTELLE MEMORIAL INSTITUTE**

**June 1, 1953**

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PURPOSE

This project has as its over-all objective the laboratory investigation of new electrochemical systems not previously used as battery power supplies.

Specifically, the program consists of three phases which will be carried on simultaneously:

- (1) Preparation of metallic carbides, borides, nitrides, germanides, phosphides, and silicides. Preparation and identification of metallic analogues to the chemical hydrides, such as alloys of the alkali metals or alkaline-earth metals with the transition metals and with elements of Groups III, IV, V, and VI of the Periodic Table. Preparation and identification of chemical combinations with extreme states of oxidation or reduction, such as selenium or tellurium in the -3, +2, +4, and +6 oxidation states or bismuth in the -3, -1, +2, +3, +4, and +5 oxidation states.

- (2) Electrochemical evaluation of compounds, alloys, and mixtures prepared in Phase (1). The physical and elementary chemical properties of all substances studied will be determined in this phase. Included will be melting points, specific resistance, stability to air, water, and other media, densities, and solubilities. Electrochemical evaluation will determine possible uses for wet, dry, reserve-type, or solid-state primary cells over a range of temperatures. Voltages will be determined with well-known or accepted electrodes as reference, and reversibility or possibilities for secondary electrodes will be studied. This phase should indicate leads for future developments toward battery power supplies.
- (3) Further investigation of promising systems resulting from the work of Phase (2) with respect to their behavior in laboratory cells, the possibility of improving performance, the use of stabilizing agents, and the determination of current-voltage characteristics at various drains and at varying temperatures. This phase will be subsidiary to the survey of Phase (2) and limited to the time and funds available.

The objectives for this report period were to establish suitable cell designs, depolarizer formulations, and test procedures for evaluation of the new electrochemical systems in aqueous media, and to begin the investigation with materials on hand.

#### ABSTRACT

The geometry of cells and of the cell components for testing new electrochemical systems was standardized. The preparation of electrodes from the new materials was standardized as regards grinding, formulation, and compression of depolarizer cakes. Procedures were established for evaluation of the new electrochemical systems in cells based upon open-circuit voltage, instantaneous voltage under increasing loads, and voltage-time relations during discharge through a constant resistance to an arbitrary cutoff voltage.

Two borides were selected as components of cells with zinc anodes. Calcium hexaboride was found to be quite inert chemically and to promote corrosion of zinc when coupled with zinc in an acid electrolyte. The couple has a potential of approximately 0.71 volt. The calcium hexaboride electrode (a cake of boride, carbon black, and electrolyte) was discharged at rather high rates without severe polarization and provided a substantial energy capacity above an arbitrary cutoff voltage. With zinc as the anode,

the closed-circuit voltage at a cathode current density of 6.3 milliamps per square inch was fairly steady at slightly over two-thirds the open-circuit voltage in preliminary tests of that type of cell. This corresponds to a 100-ohm load. The energy capacity, determined from discharge through 100 ohms to a cutoff voltage of 0.2 volt, varied from approximately 0.15 to 1.8 watt-minutes per gram of calcium hexaboride for standard-size cells containing  $\text{CaB}_6$  of varying particle size.

The other "boride" studied was ferroboration. The chemical activity of this material was high in both acid and basic electrolytes, so it is not a suitable electrode material without corrosion inhibitors. However, fresh cells made with ferroboration cathodes and zinc anodes polarized only 20 millivolts on instantaneous load through 50 ohms (5.8 milliamperes per square inch). Their open-circuit voltage was approximately 0.4 to 0.5 volt, depending on the boron content of the ferroboration used. Their capacity was nil after one day of storage. It is not within the scope of the immediate program to develop an inhibitor and extend the shelf life of this electrochemical system. However, massive ferroboration electrodes (rather than powder) should be tested using an electrolyte containing soluble chromate to evaluate this new electrode material adequately.

### CONFERENCES

On March 26, 1953, Drs. McGraw and McCallum visited the Squier Signal Laboratories to confer with representatives of the Signal Corps. Representing the latter organization were Messrs. Daniels, Shorr, Shaperio, and Luden.

Technical details for the initial conduct of the research were discussed. In addition, it was agreed that no development of interesting leads should be carried on during the early portion of the program, but, rather, a screening or surveying of a wide variety of compounds.

Dr. McGraw attended the Signal Corps Battery Research and Development Conference at Asbury Park, New Jersey, on May 13 and 14, 1953, at the invitation of the Signal Corps Engineering Laboratory. During this conference, much information of value to this project was obtained.

### BACKGROUND INFORMATION

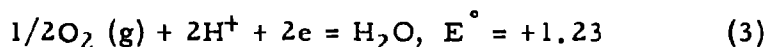
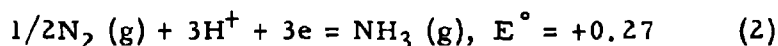
Most of the electrochemical systems for which thermochemical data are available have been studied for suitability as battery power supplies. Hundreds of combinations of electrodes have been proposed, constructed, and tested. The physical, chemical, electric, and economic

suitabilities of the components of these systems have been evaluated at least superficially.

This program proposed that there were potentialities for new batteries of specialized design for applications which will use materials only recently available or relatively unknown as electrode materials. Suggestions for new materials are based upon recognized physical and chemical principles and upon rather meager thermochemical data.

Examination of the Periodic Table for possible new electrochemical systems reveals that some elements now considered unconventional for battery use generally are believed to be too inert. For example, the direct or indirect reduction of carbon as a source of electric power at low temperature is a desirable goal. However, the high energy of the carbon-to-carbon bond requires activation energies so large that reactions involving the free element do not occur at a useful rate at low temperature. A similar situation exists with elemental silicon, boron, nitrogen, and other inert elements.

Carbon, silicon, boron, nitrogen, and oxygen are fairly good oxidizing agents, judging from the partial list of free-energy changes involved in the following reactions:



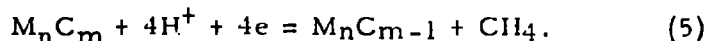
However, in view of the high energy of the interatomic bonds in these elements, the activation energy is so large that, even at high overvoltage, the elements (with the exception of oxygen) cannot be reduced at low temperature. For probably the same reason, carbon is not hydrolyzed at room temperature, although it could be expected to react with water according to the following reaction to give appreciable partial pressures of gaseous products:



These elements can be activated by conversion to carbides, silicides, borides, and nitrides in much the same way as oxygen is activated at an "inert" carbon electrode or as hydrogen is activated by adsorption on or by hydride formation with certain metal electrodes. This change from useless to useful chemical agents involves a reaction producing "compounds" with oxidation potentials differing from those of the elements.

The attendant reduction in activation energy required to hydrolyze the carbon, silicon, boron, etc., in the carbides, silicides, borides, etc., is high. Many of the compounds can be hydrolyzed easily at room temperature.

If this enhanced chemical activity of carbon in carbides is extended to oxidation-reduction reactions, an electrochemical reaction of the following type may prove practical:



As a guiding principle in electrode kinetics, the lowering of activation energy is associated tentatively with a decrease in covalent-bond strength. For example, the standard heat of formation of  $C_2$  (g) is very high (235 kilocalories per mole), and the covalent-bond energy for carbon\* in its compounds is high (80 kilocalories per mole). However, the heats of formation of many carbides are very low, as are the covalent-bond strengths. For example, the heats of formation of  $CaC_2$ ,  $Al_4C_3$ , and  $WC$  are fairly close to zero. Many molecules having low covalent-bond strengths also have a low energy of activation (or overvoltage) required for oxidation or reduction. Elements with high covalent-bond strengths have high activation energies in their electrochemical reactions. Hydrogen is difficult to oxidize electrochemically unless it reacts to form alloys with the metal electrode. It has a high bond strength (103 kilocalories per mole).

Thermochemical data are not available for many of the electrode materials proposed here. The free energies of formation of the compounds from their elements are mostly rather low, as evidenced in some cases by the thermal dissociation of carbides to liquid melt and graphite. This is accomplished more easily than thermal dissociation of elemental carbon. Also, because the free energies of formation of these compounds are low, their oxidizing power is expected to be about the same as the oxidizing power of the elemental carbon, boron, etc. For example,  $CaB_6$  is a weak oxidizing agent characteristic of boron, rather than a strong reducing agent characteristic of calcium. For this reason, cell voltages are not expected to be over one volt when zinc or magnesium anodes are used. Cell reactions are not known, but the reduction of carbides, borides, etc., is expected to follow Equation 5.

Only those compounds which do not hydrolyze will be useful in batteries. Calcium hexaboride, for example, does not hydrolyze readily, but is cathodic when coupled with zinc. This is indicative of lack of the covalent-bond strength which keeps elemental carbon or boron from being active cathodes.

Metal carbides could be produced cheaply on a large scale, are easy to handle, and are noncritical.

Another group of materials which might be of interest as reducing agents in battery systems is the group of metallic analogues of the chemical hydrides in which the hydrogen is replaced by an alkali or alkaline-earth metal. A few examples of such "compounds" might be  $SbNa_3$ ,  $As_2Ca_3$ , etc. The electrochemistry of such compounds is unknown, but it may be possible to utilize the overly active metals as anodes in the form of such compounds

\* Pitzer, K. S., J. Am. Chem. Soc., 70, 2140 (1948).

and yet retain the electrochemical properties of the parent element to some extent.

## FACTUAL DATA\*

### Introduction

A number of exploratory experiments were made in order to establish whether the electrical properties of borides would permit the use of cell designs and fabrication familiar to the dry-cell industry. These tests were also designed to establish the order of magnitude of electrode potentials and of useful discharge rates for borides.

### The Electrochemical Activity of Calcium Hexaboride

#### Experiment 8011-1A

The first new electrode material tested was calcium hexaboride. It was chosen for its relative chemical stability in aqueous solutions.

Its electrochemical activity as a cathode was established by observation of the corrosion of zinc coupled with the boride in an acid electrolyte.

Gritty  $\text{CaB}_6$ \*\* was ground in a mortar until it was reduced to a fine powder. A paste was prepared with 0.9 gram of the powdered boride, 0.1 gram of Shawinigan Black (50 per cent compressed grade), and electrolyte of the following composition:

$\text{NH}_4\text{Cl}$	26 per cent by weight
$\text{ZnCl}_2$	8.8 per cent by weight
Water	65.2 per cent by weight

The paste was pressed into a cake (3/4-inch diameter x 1/16 inch thick) on a piece of battery-grade zinc of the same diameter and 0.013 inch thick. Filter paper on top of the paste absorbed electrolyte forced from the paste during the pressing operation. The zinc-calcium hexaboride couple was stored overnight.

\* The data for this report are recorded in Battelle Laboratory Record Books No. 8011, pages 1-26, and No. 8012, pages 1-12.

\*\* Purchased from A. D. MacKay, Incorporated, 198 Broadway, New York 38, N. Y. Vendor's analysis - Ca 29.6%; B 54.1%.

Within a storage period of 16 hours, all the zinc in the couple prepared as described above was oxidized, indicating that the chemically stable boride was a new and active cathode material.

Preliminary Evaluation of the Discharge  
Characteristics of the Zinc-Calcium Hexaboride Couple

Experiment 8011-2A

A simple cell was constructed using a depolarizer cake and zinc anode like those described in Experiment 8011-1A. The cell was fashioned from these components by separating the anode from the cathode by two circles of filter paper. These components were pressed together between a glass microscope slide and a piece of graphite. The glass slide rested on the zinc and the graphite contacted the cathode (depolarizer cake). A narrow strip of zinc served as external lead to the zinc anode. The area of the cake was 4.25 square inches and its volume was 0.028 cubic inch.

The open-circuit voltage of the cell was 0.682 volt. The terminal voltage of the cell discharging through a resistor (nominally rated as 1000 ohms) was 0.640 volt. When discharged through a resistor (nominally rated as 100 ohms), the cell polarized rather rapidly for ten minutes and then leveled off at an approximately one milliwatt power level, as shown in Table 1.

TABLE 1. PRELIMINARY CONTINUOUS DISCHARGE TEST  
ON SMALL  $\text{CaB}_6$  CELL

Time, minutes	Load, ohms	Closed Circuit Voltage, volt
0	100	0.425
5	"	0.382
10	"	0.374
15	"	0.365
20	"	0.360
30	"	0.360
50	"	0.355
105	"	0.310

These results were encouraging and led to the next similar test of a cell of larger area and larger cake volume.

Experiment 8011-4A

A depolarizer cake of the same composition as in Experiments 8011-1A and -2A was formed to 1-inch diameter and 3/32-inch thickness. The cake area was 0.79 square inch and its volume was 0.074 cubic inch. It was inserted in a 1-inch-diameter Lucite tube plugged with a graphite cap, and separated from a circle of battery grade zinc by a 1/8-inch-thick pad of filter paper pulp moistened with the electrolyte.

The cell had an open-circuit voltage of 0.790 volt and the 100-ohm-drain test resulted in approximately 5 milliwatts power for 2-1/2 hours.

TABLE 2. PRELIMINARY CONTINUOUS DISCHARGE  
TEST ON LARGER  $\text{CaB}_6$  CELL

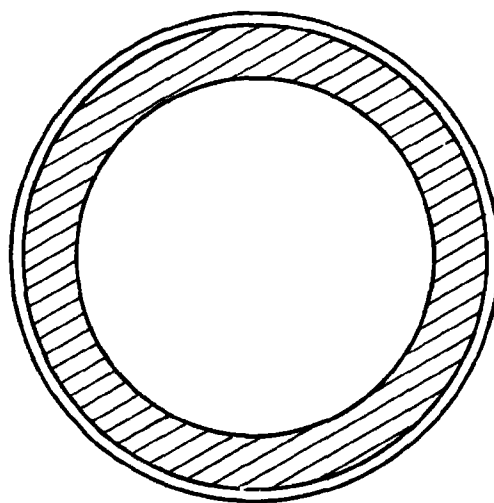
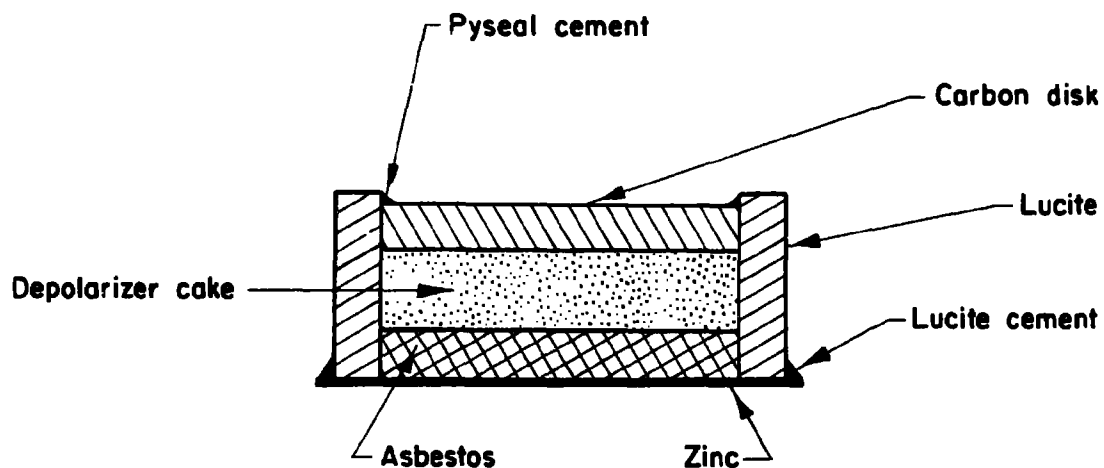
Time, hours	Closed Circuit Voltage, volt	Continuous Discharge, ma/in. <sup>2</sup>
0.0	0.740	9.9
0.5	0.728	9.3
1.0	0.708	9.0
1.5	0.691	8.8
2.0	0.672	8.5
2.5	0.649	8.3

These preliminary tests were done without calibrated electrical components and without regard for the particle size of the boride or for the formation pressure of the electrodes. The results were satisfactory and indicated the need for precise evaluation of the effects of particle size and formation pressure on the discharge characteristics of the new boride cathode.

Design of Standard Test Cell and  
Fabrication of Cell Components

A test cell of standard dimensions was chosen so that subsequent evaluations of new electrodes would not be influenced by variations in the geometry of cells.

The result was the cell design shown schematically in Figure 1. The cell consists of a one-inch-ID Lucite tube, 1/2 inch long. One end is sealed with Lucite cement to a 13-mil-thick circle of battery-grade zinc.



Note: Twice actual size

FIGURE 1. SCHEMATIC DRAWING OF STANDARDIZED EXPERIMENTAL CELL

A-6046

The other components are a 1/8-inch-thick asbestos-fiber separator saturated with electrolyte, a 1/8-inch-thick cathode cake, and a 1/8-inch-thick graphite circle for making electrical contact with the cathode. Pyseal\* was used to effect a seal between the carbon disk and the Lucite cell wall. The separators and cathode cakes were slightly variable in thickness, as well as in composition.

The cathode cakes were all made to the same weight, including active material, carbon, and electrolyte. Consequently, their thicknesses varied with the density of the various new active cathode materials under test. They were prepared by compression of the wet mix onto the graphite conductor seated in a one-inch-diameter Lucite die. The die had a hole in the bottom to permit electrolyte to escape, as well as around the edges of the porous and loosely fitting graphite disk during the compression stroke on an arbor press. Approximately 800 psi were applied to the cake by a one-inch-diameter Lucite piston activated by a lever with a 12-to-1 mechanical advantage. This choice of pressure is discussed in the next section.

The separators were prepared from a thick slurry of fibrous asbestos soaked in electrolyte. A portion of the slurry was compressed lightly to an approximately 1/8-inch-thick disk in a one-inch-diameter vertical cylinder having its open end resting on absorbent paper. This was a provisional separator structure. The resistance of such separators was not high, but the possibility of polarization of cathodes that imbibe electrolyte from the separator and swell to a greater specific volume was evident. Under such conditions, the cakes would have the poor electronic conductivity characteristic of fabrication under lower pressure.

#### The Effect of Pressure on Polarization Characteristics of Cathode Cake Mixes

Preliminary attempts to relate the polarization of calcium hexaboride cakes to the particle size of the boride were not definitive when low and unmeasured pressures were used to form the cakes. For this study the electronic resistance in the cake should be low and variations in electronic resistance should not prevail over the polarization changes attendant upon variation of particle size. To arrive at such a condition, some minimum or unvaried high pressure was required for cake fabrication.

To establish the approximate pressure required, bobbins from commercial Leclanche' dry cells were carefully dissected and cut to fit the standard one-inch-diameter test cell. Other samples of the same mix were crumbled and compressed again into cakes fitting the test cell. These cells were discharged continuously through 100 ohms to determine what

\* "Pyseal" is a thermoplastic cement manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania.

pressure was sufficient to realize equally good performance from the re-compressed cakes and the cakes which had been left intact.

Between 500 and 800 psi were sufficient to prevent abnormal polarization under 100-ohm load. Approximately 800 psi was chosen as the standard pressure to use for the formation of cakes of new electrode materials.

Evaluation of  $\text{CaB}_6$  as an Electrode Material  
and Influence of Particle Size on Results

Experiment 8011-16A

Calcium hexaboride is quite stable against chemical attack by acid and basic aqueous solutions, but is electrochemically active to the extent that it promotes rapid corrosion of zinc when coupled with it in acid solution.

Determination of the electrochemical energy of this couple with zinc was done by discharge of standard-size test cells, as described in previous sections. The cathodes of the cells were cakes of the following composition, compressed to 800 psi:

	<u>Grams</u>
$\text{NH}_4\text{Cl}$	0.43
Shawinigan Black (50 per cent compressed)	0.51
$\text{CaB}_6$	3.73
Electrolyte	2.6

The composition of the electrolyte was:

	<u>Parts by Weight</u>
Water	15
$\text{NH}_4\text{Cl}$	7
$\text{ZnCl}_2$	2

Six grams of wet mix were used for each cathode.

The tests were designed to show the effect of the particle size of the boride on its electrical characteristics. The boride was ground and separated with an Infrasizer\* to provide enough material for seven cells covering five ranges of particle size. Figures 2, 3, 4, and 5, and Table A-1 in the Appendix give the results of the tests.

\* The Infrasizer, Infrasizers Limited, Toronto, Canada.

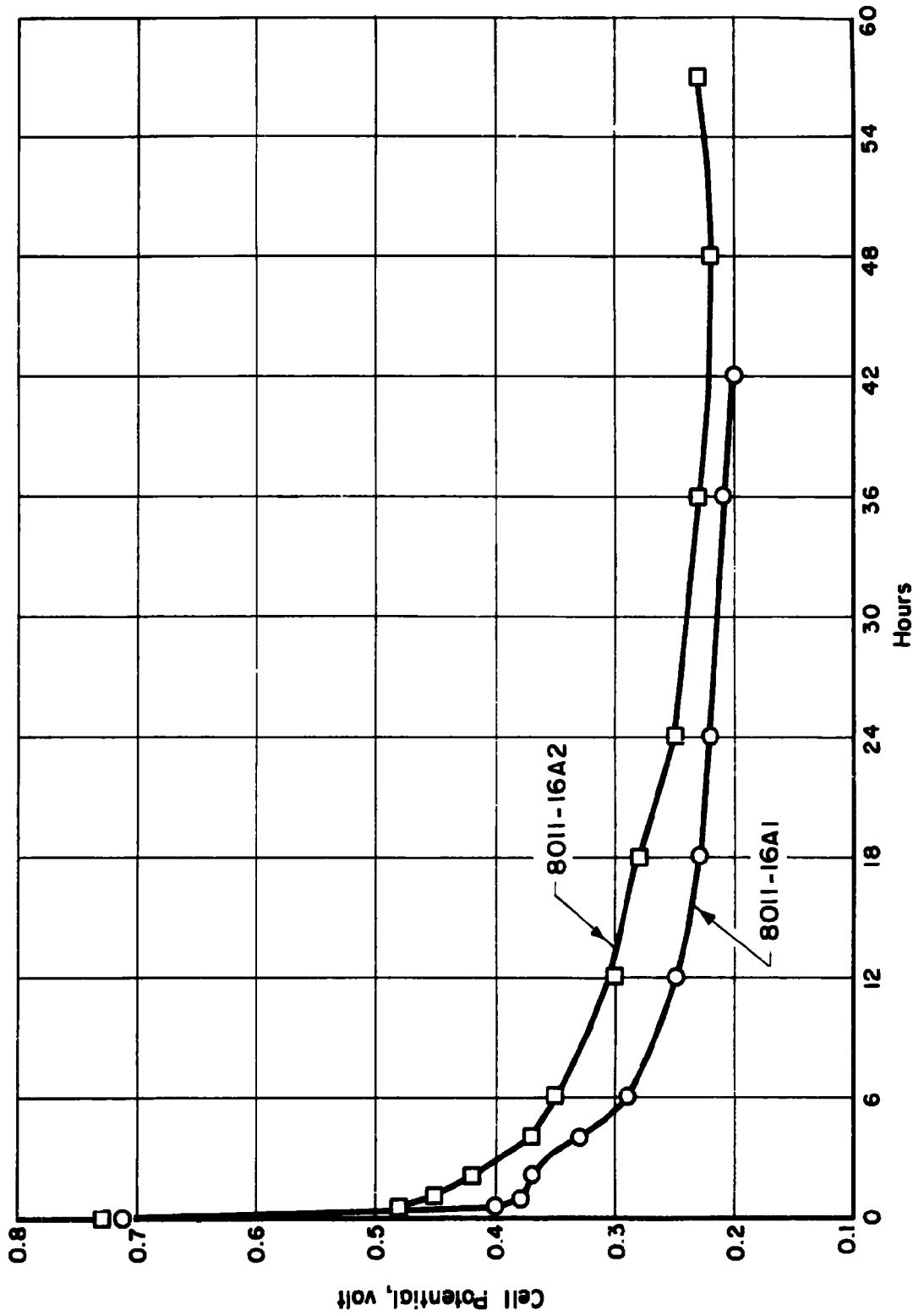


FIGURE 2. CONTINUOUS-DISCHARGE CHARACTERISTICS OF  $\text{CaB}_6$  CELLS DRAINING THROUGH A 100-OHM RESISTANCE; TEMPERATURE, 100 F; PARTICLE SIZE, 50 TO 117 MICRONS

A-6047

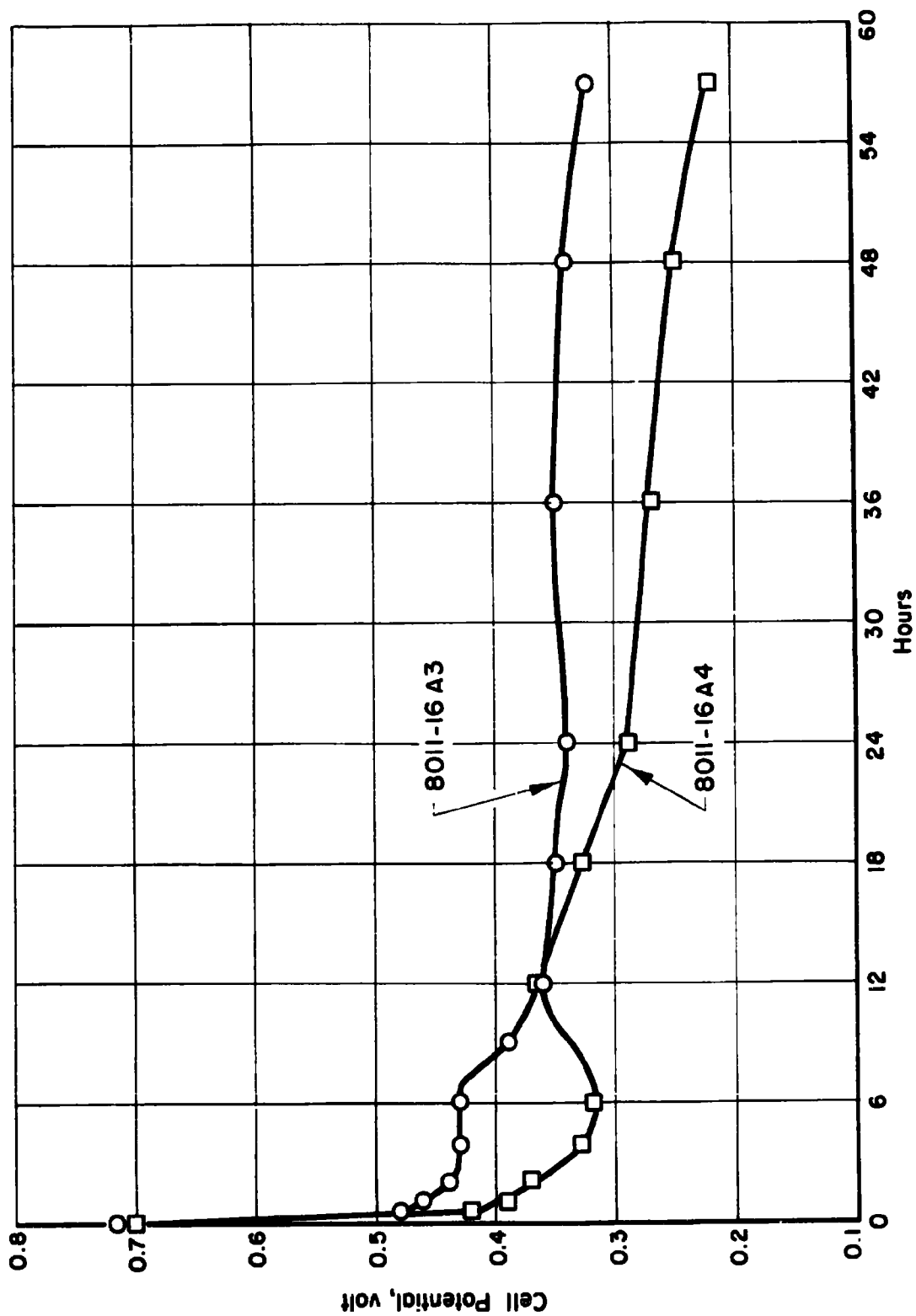


FIGURE 3. CONTINUOUS-DISCHARGE CHARACTERISTICS OF  $\text{CaB}_6$  CELLS DRAINING THROUGH A 100-OHM RESISTANCE; TEMPERATURE; 100 F, PARTICLE SIZE, 30 TO 69 MICRONS

A-5048

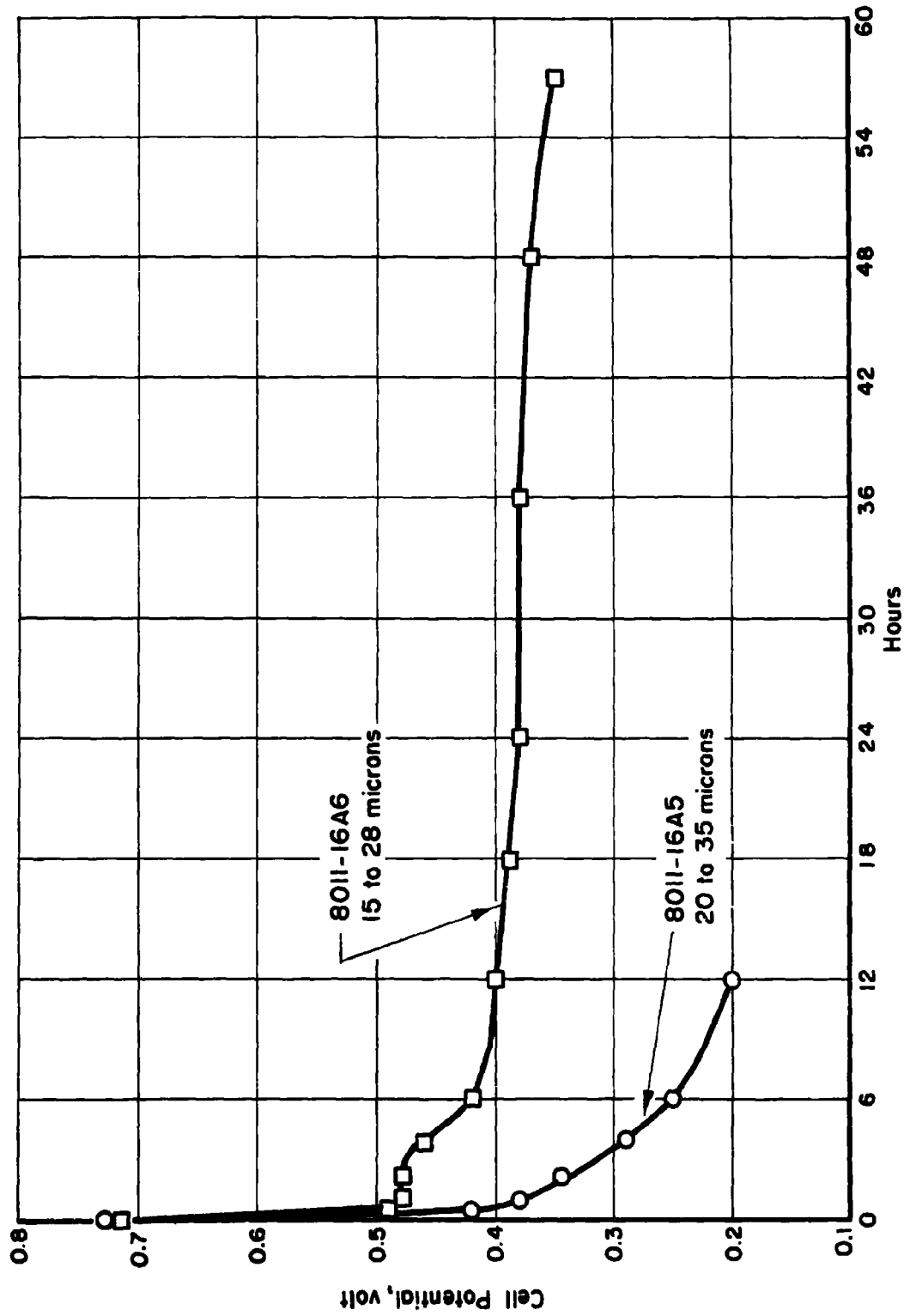


FIGURE 4. CONTINUOUS-DISCHARGE CHARACTERISTICS OF  $CdB_6$  CELLS DRAINING THROUGH A 100-OHM RESISTANCE; TEMPERATURE, 100 F; PARTICLE SIZES AS INDICATED

A-6049

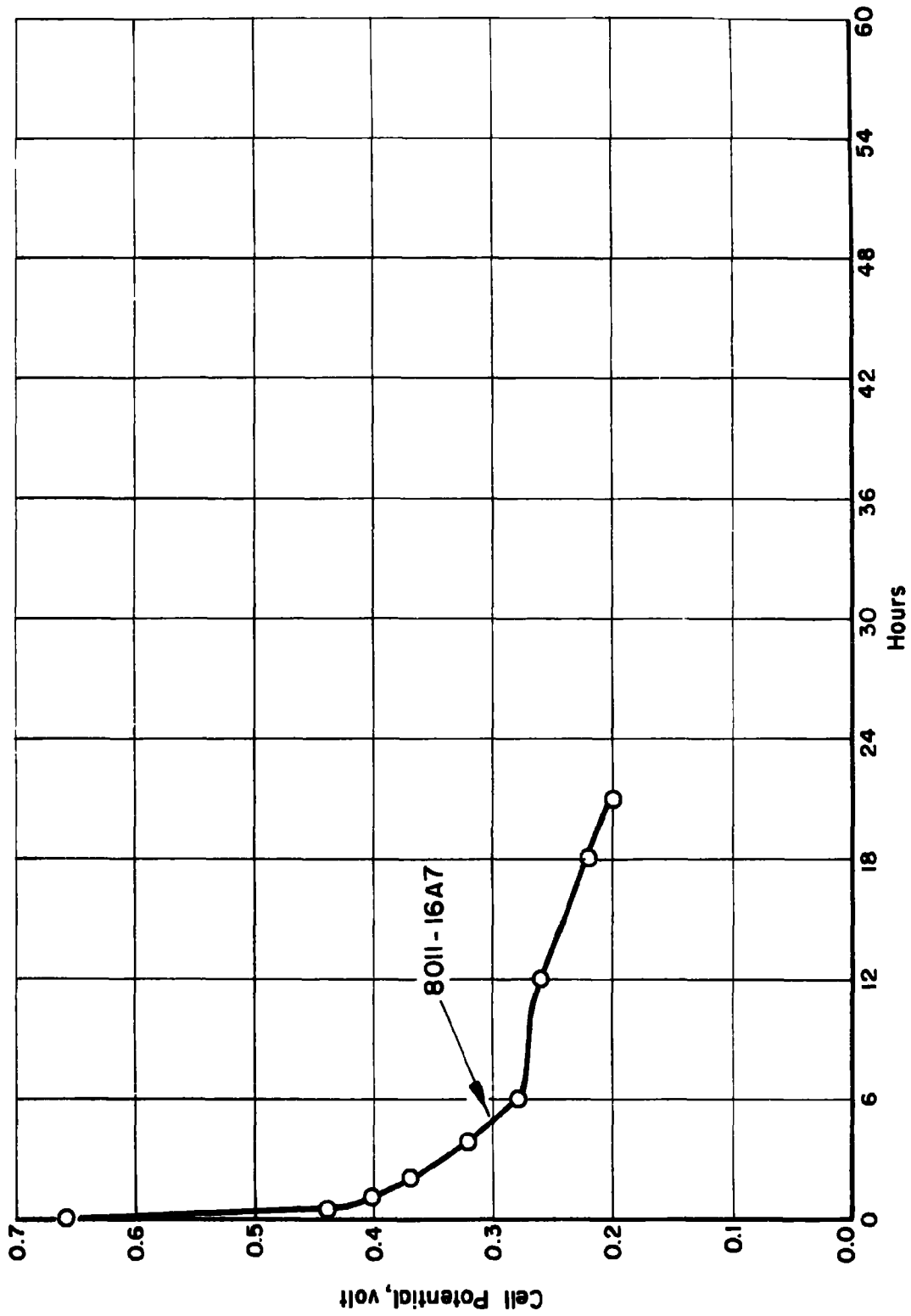


FIGURE 5. CONTINUOUS-DISCHARGE CHARACTERISTICS OF  $\text{CoB}_6$  CELLS DRAINING THROUGH A 100-OHM RESISTANCE; TEMPERATURE, 100 F; PARTICLE SIZE, <12 MICRONS  
A-6050

Table 3 shows that there was no consistent variation of energy capacity of the cells with the particle size of calcium hexaboride in the cathode. Capacities were obtained by graphical integration.

TABLE 3. WATT-MINUTE CAPACITY OF  $\text{CaB}_6$  CELLS WITH CATHODES MADE FROM PARTICLES OF DIFFERENT SIZES

Cell No.	Particle Size, microns	Capacity to 0.2-Volt Cutoff, watt-minutes	Capacity per Gram of $\text{CaB}_6$ , watt-minutes
16A1 16A2	50 to 117	2.0 (avg)	0.55 (avg)
16A3 16A4	30 to 69	4.0 (avg)	1.1 (avg)
16A5	20 to 35	0.6	0.16
16A6	15 to 28	6.6	1.8
16A7	< 12	1.1	0.29

Apparently, capacities were related more closely to variations in the procedure of cell construction than to variations in particle size.

Considerably more testing of this cell could be done with lower discharge rates to obtain higher energy capacities and low polarization. The 100-ohm-discharge test was a rather high rate for this cell. Preliminary Experiment 8011-4A had indicated that a 100-ohm load would not be too severe.

#### Evaluation of Iron Boride as an Electrode Material

##### Experiment 8011-19

Three lots of ferroboron\* were available. The boron contents\*\* were as follows:

- \* Lots 382 and 403 from Molybdenum Company of America;  
Lot 383 from Union Carbide and Carbon Corporation.
- \*\* Vendors' analyses.

	<u>Per Cent Boron</u>
Lot 382	19.5
Lot 383	18.0
Lot 403	10.8

Portions of each lot were ground separately until all the material passed a 200-mesh sieve. Four cells were made from each lot using acid electrolyte. One of each four was intended for storage.

Wet mixes were formulated as given in Table 4 and were used to make 6-gram cathode cakes for the 12 cells.

TABLE 4. CAKE-COMPOSITION DATA FOR ACID-ELECTROLYTE FERROBORON CELLS

Cell No.	Ferroboron Lot No.	Composition, grams			Electrolyte (Same as for Test 8011-16)
		Iron Boride	Shawinigan Black (50% Compressed)	NH <sub>4</sub> Cl	
19A1 to 19A4	382	34.65	4.33	5.20	22.1
19B1 to 19B4	383	44.13	5.52	6.62	28.14
19C1 to 19C4	403	38.29	4.7	5.75	24.4

All three wet mixes heated up considerably during mixing, so more cells were made using basic electrolytes for 6-gram cakes and the separators as given in Tables 5 and 6.

TABLE 5. CAKE-COMPOSITION DATA FOR ALKALINE-ELECTROLYTE (NO ZINC) FERROBORON CELLS

Cell No.	Ferroboron Lot No.	Composition, grams		
		Iron Boride	Shawinigan Black (50% Compressed)	Electrolyte (31% KOH)
23A1 to 23A3	382	20	2.5	13.0
23C1 to 23C3	383	20	2.5	13.0
23B1 to 23B3	403	20	2.5	13.0

TABLE 6. CAKE-COMPOSITION DATA FOR ALKALINE-ELECTROLYTE (WITH ZINC) FERROBORON CELLS

Cell No.	Ferroboron Lot No.	Composition, grams		
		Iron Boride	Shawinigan Black (100% Compressed)	Electrolyte (35% KOH-5% ZnO)
25A1 and 25A2	382	20	2.5	15.0
25B1 and 25B2	383	20	2.5	15.0
25C1 and 25C2	403	20	2.5	15.0

The results of the electrical tests on the ferroboration cells are given in Tables A-2, A-3, and A-4 in the Appendix. They illustrate the chemical activity of ferroboration in acid and basic electrolytes, and the very slight polarization of ferroboration cathodes under heavy load. They also indicate a linear increase in the cathode potential of ferroboration with increasing boron content, as illustrated in Figure 6. This was evident only when a basic electrolyte containing zinc was used in the wet mix and in the separators.

The continuous-discharge tests, initiated 18 hours after cell assembly, are not instructive because much of the ferroboration had been chemically decomposed by the electrolyte after that length of storage. The capacity of the cells was obviously too small to warrant calculation.

This work will be repeated with massive ferroboration cathodes in the presence and absence of soluble chromate in the electrolyte. This procedure should reduce chemical attack on the cathode material. The instantaneous closed-circuit voltages measured under varying loads (Tables A-2, A-3, and A-4) indicate that the standard 100-ohm-discharge test will not be too severe on these cells if chemical stability is achieved with the inhibitor.

### Apparatus and Methods for Testing Cells

#### Recording Battery Tester

The battery tester used in this work is pictured in Figure 7. A single basic circuit is used for each of twelve positions shown on the test board. The batteries are inserted in the spring bronze clips, and either open-circuit potentials or potentials under load can be measured. The choice is controlled by individual toggle switches.

The test board is kept in a thermostatically controlled oven with the temperature set for 100 F. The usual "room temperature" of 77 F (25 C) would have been more difficult to maintain because laboratory temperatures during the summer frequently rise to 95 F.

For open-circuit-potential measurements, the toggle switch is thrown to the "up" position. The terminals for the "up" positions of all the switches are connected in parallel. Therefore, only one open-circuit potential can be measured at one time. Figure 8 shows a wiring diagram of three of the twelve components of the circuit.

The open-circuit potentials are measured with a Leeds and Northrup No. 7664 vacuum-tube pH meter which is easily changed over for potential measurements. It is an ideal instrument for open-circuit potentials because of its high internal resistance (about  $10^9$  ohms).

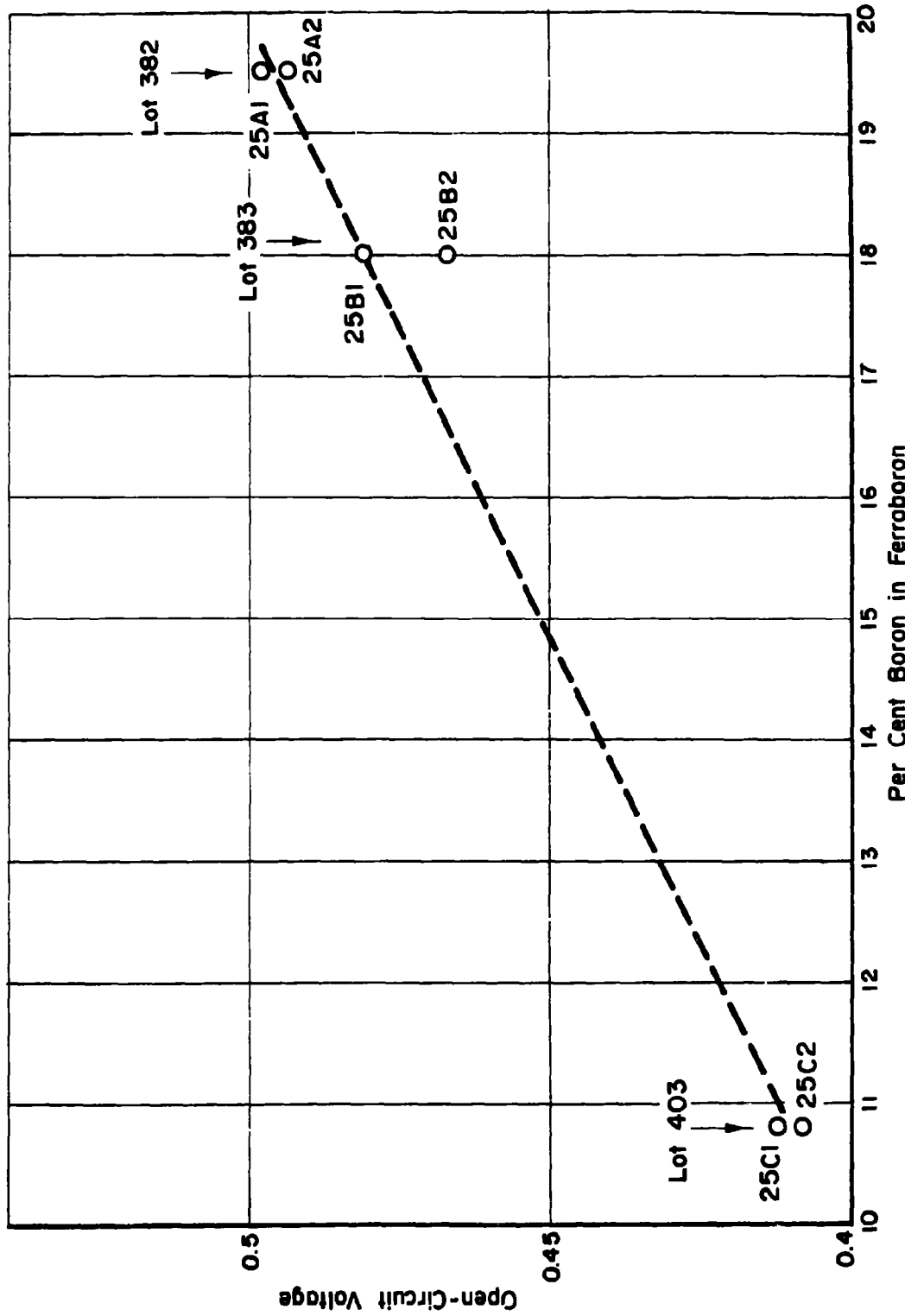
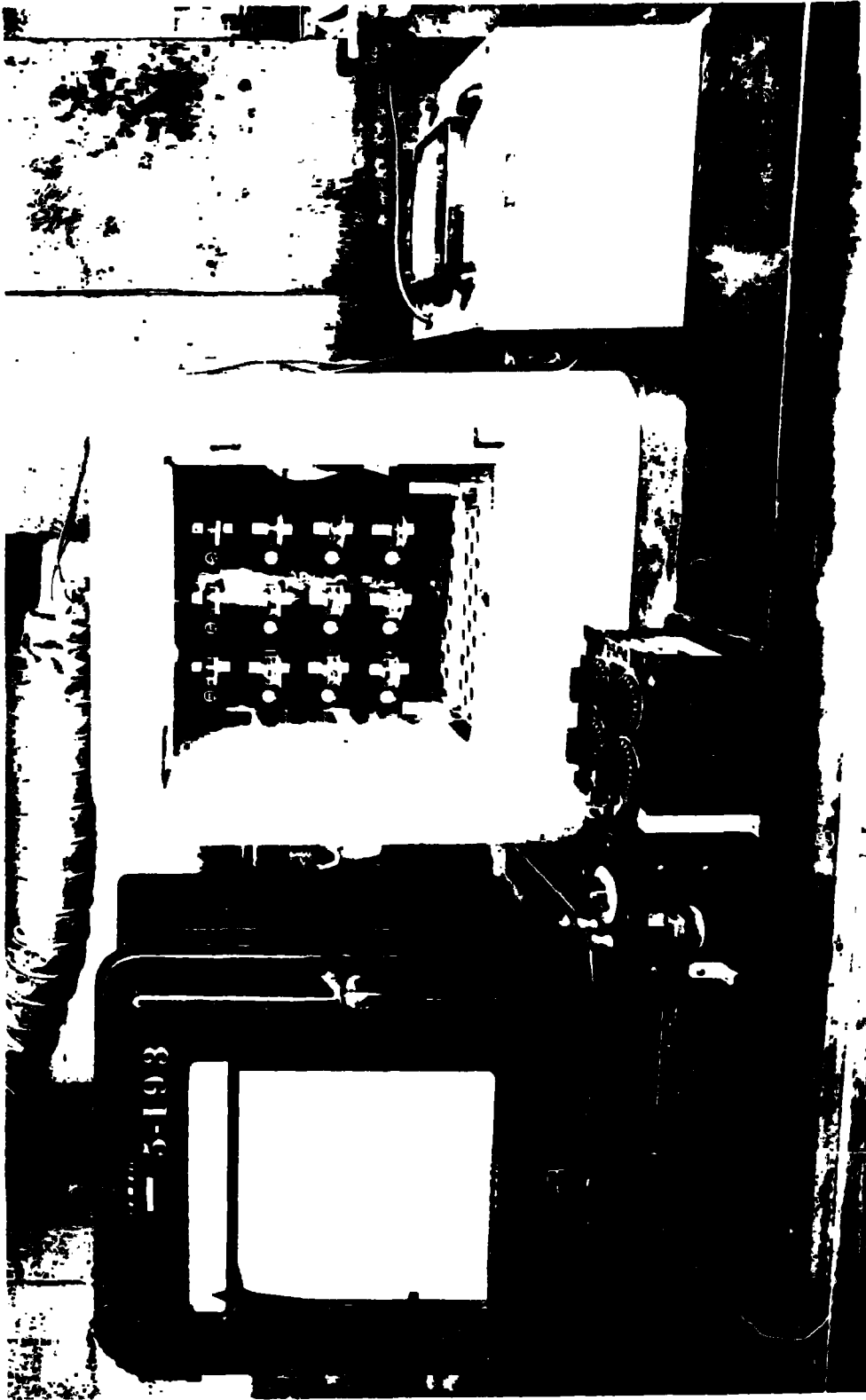


FIGURE 6. RELATION BETWEEN BORON CONTENT OF FERROBORON AND OPEN-CIRCUIT VOLTAGE IN CELLS WITH ALKALINE ELECTROLYTE CONTAINING ZINC

A-351



N2492

FIGURE 7. RECORDING BATTERY TESTER

The door of the constant-temperature oven was removed to facilitate taking the picture.

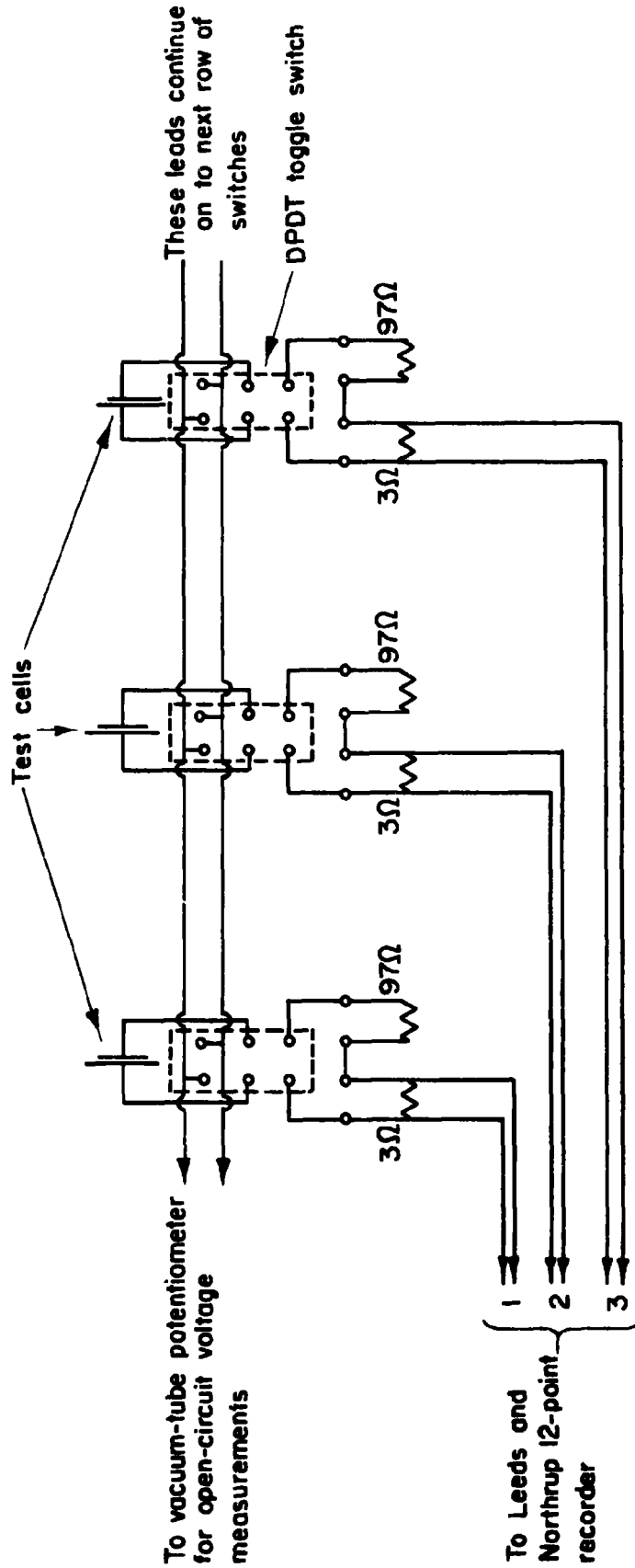


FIGURE 8. CIRCUIT DIAGRAM FOR THREE OF THE TWELVE COMPONENTS OF THE RECORDING BATTERY TESTER

A-6082

When the toggle switch is in the "down" position, the test cell discharges through two resistors totaling 100 ohms. One resistor is 97 ohms and the other is 3 ohms. The IR drop through the 3-ohm resistor is utilized to activate the indicator on the Leeds and Northrup 12-point recorder. A 12-pair cable runs from the back of the test board to the recorder.

The recorder prints a dot with identifying number for each cell once every twelve minutes on a chart which moves 3 inches per hour. The maximum voltage which can be recorded is about 1.65 volts. The scale shown on the recorder in Figure 7 does not read directly in potential values. A conversion factor must be applied. However, a special scale has been made for taking the values from the chart.

Just above the constant-temperature oven in Figure 7 is a flexible tube which is connected to an exhaust system. Any toxic fumes resulting from the cell reactions will be drained off through the small opening in the oven.

Figure 9 shows a closeup of the back of the test panel. Standard items were used throughout. The toggle switches are of the DPDT type with neutral center positions. The terminal strips are of the double-screw type.

The 97-ohm resistors were made from IRC\* or Ohmite\*\* 100-ohm wire-wound resistors having an adjustable tap. The adjustable taps were set to 97 ohms  $\pm$  1 per cent at the Battelle Instrument Laboratory. In some cases, the total resistance fell within the tolerance and the adjustable tap was not used. The 3-ohm resistors were made in the same way, using resistors whose total value was 5 ohms. These, too, were set within 1 per cent.

Stiff wire leads were soldered to the resistors and fork-type terminals were fitted to the outer ends of the wires. The resistors are then easily "plugged in" or removed from the terminal strips. Thus far, only 100-ohm resistances have been used, but this setup makes it easy to change over to higher or lower resistances.

After fitting the resistors with the wire leads, they were recalibrated.

#### Methods of Testing Experimental Cells

The cells were clamped on the test board at about 4:30 p.m., and open-circuit voltages were taken immediately.

\* International Resistor Company, Philadelphia 8, Pennsylvania.

\*\* Ohmite Manufacturing Company, Chicago, Illinois.

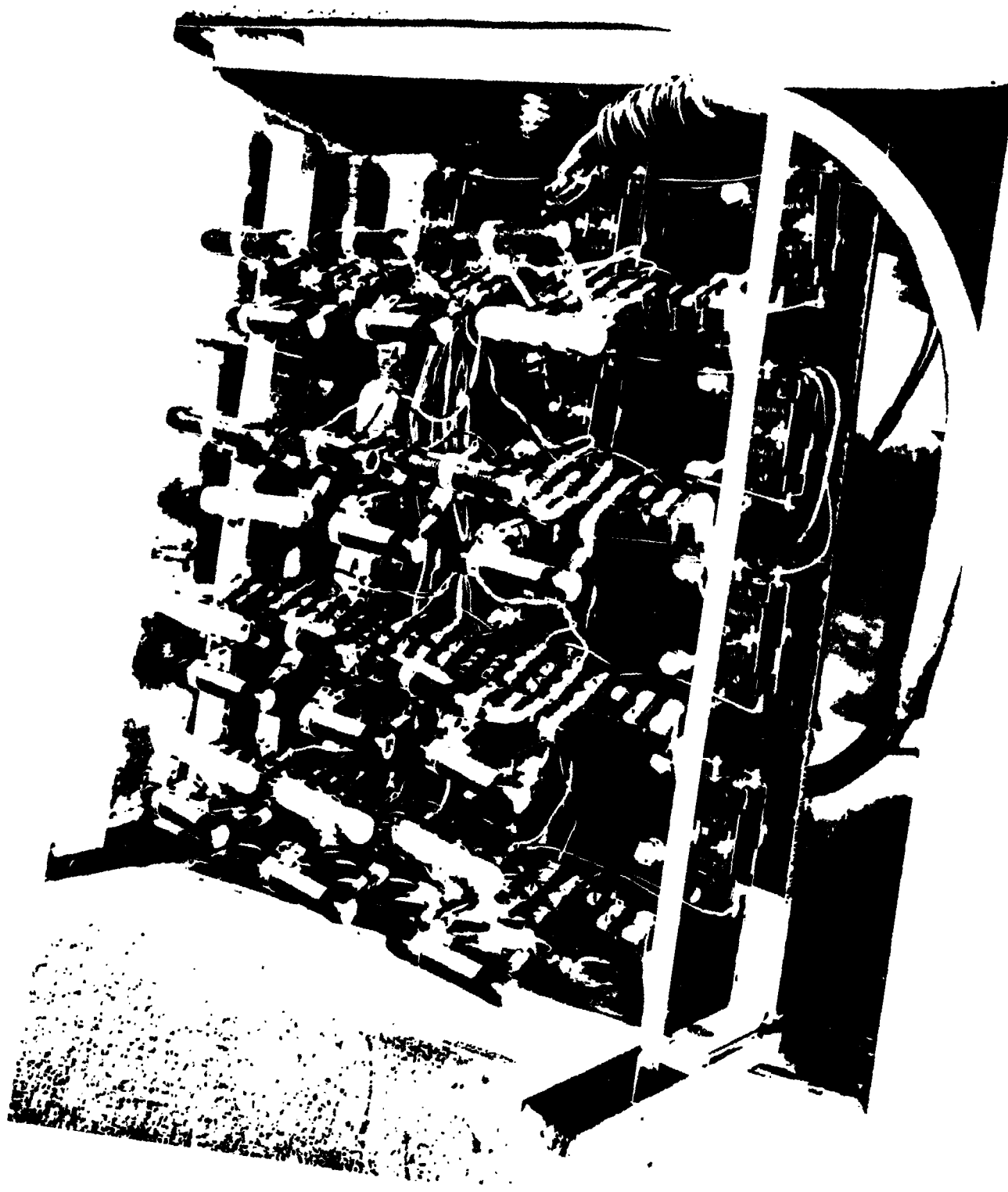


FIGURE 9. BACK OF BATTERY-TESTER PANEL  
SHOWING RESISTOR ARRANGEMENT

N2493

BATTELLE MEMORIAL INSTITUTE

Overnight the cells came to temperature, and at 8:00 a.m. of the following day the open-circuit voltages were taken once more. The recorder was then turned on and each cell was started discharging one minute before the recorder printed its potential. Therefore, each initial voltage record is printed on the chart one minute after the cell started discharging.

The cells were discharged continuously through the 100-ohm resistances until the voltage fell below some arbitrary value, which was 0.2 volt in the case of the  $\text{CaB}_6$  and ferroboron batteries.

#### Apparatus for Making Instantaneous Closed-Circuit Voltage Measurements

Resting in front of the constant-temperature oven in Figure 7 is the apparatus used in making preliminary instantaneous closed-circuit measurements.

A five-place rotary switch was used for selecting either one of two fixed resistances or a variable resistance. The fixed resistors were 100,000 ohms and 50,000 ohms, respectively, and the variable resistance was a Leeds and Northrup decade resistance box having a maximum resistance of 10,000 ohms. Two of the switch positions can be used for open-circuit measurements. The battery was inserted in the spring bronze clips and the vacuum-tube pH meter was connected to the binding posts on the selector-switch box.

### CONCLUSIONS

Calcium hexaboride appears to hold promise as a cathode-depolarizer material for use in primary cells. In fabricating the depolarizer cakes, pressures of approximately 800 psi were found to be necessary to prevent severe polarization. No correlation was found between calcium hexaboride particle size and cell capacity.

Ferroboron ("iron boride") is too reactive chemically and probably cannot be used as a depolarizer material because of its short shelf life. Iron boride may be useful where the electrolyte is added just before the cell is to be used, or where the iron boride cathode is in massive form, and the electrolyte contains an inhibitor. It is necessary, in cells with alkaline electrolyte, and possibly in those with acid electrolyte, to have zinc in the electrolyte in order to obtain reproducible open-circuit potentials. The open-circuit potentials increase as the boron content of the ferroboron increases.

### PROGRAM FOR NEXT INTERVAL

The same technique used to evaluate the  $\text{CaB}_6$  alloy and iron-boron alloys as electrode materials will be used on a small number of carbides, silicides, and nitrides. This will establish the general trend of chemical activity, cathode potential, and cathode polarization as functions of chemical composition of new electrode materials.

Solid ferrobaboron cathodes will be tested in chromate-containing electrolyte to determine their capacity when chemical action is under control.

### IDENTIFICATION OF PERSONNEL

Dr. L. D. McGraw, Principal Physical Chemist, is a graduate physical chemist specializing in electrochemistry, electrode kinetics, and thermodynamics. He has conducted research in these fields for over six years, and has guided the theoretical study of the mechanism by which hydrogen enters metals and of electrode processes occurring at cathodes and anodes.

Mr. A. B. Tripler, Jr., Principal Electrochemist, is a graduate chemist with over 12 years of experience in the fields of alloy electro-deposition, corrosion, electrode-potential studies, and inorganic chemistry.

Dr. C. L. Faust, Supervisor, Electrochemical Engineering Research Division, is a graduate chemical engineer and physical chemist, specializing in electroprocesses, and is registered as a Chemical Engineer in the State of Ohio. He has conducted and supervised electroprocess research and development for twenty-two years.

During the period covered by this report, the man-hour labor distribution for the key technical personnel assigned to this project was as follows:

	<u>Hours</u>
L. D. McGraw	297
A. B. Tripler, Jr.	307
C. L. Faust	34

LDM:ABT:CLF/bas

## APPENDIX

This Appendix contains tabulated data of electrical tests on calcium hexaboride and ferroboron cells.

TABLE A-1. OPEN-CIRCUIT VOLTAGE AND POTENTIAL UNDER CONTINUOUS DISCHARGE FOR CALCIUM HEXABORIDE CELLS

Experiment 8011-16A

Cell No:	16A1	16A2	16A3	16A4	16A5	16A6	16A7
Particle Size of CaB <sub>6</sub> , microns:	50 to 117	50 to 117	30 to 69	30 to 69	20 to 35	15 to 28	<12
Open-Circuit Voltage, volt:(1)	0.725	0.737	0.723	0.733	0.742	0.704	0.646
Open-Circuit Voltage, volt:(2)	0.713	0.728	0.714	0.702	0.724	0.715	0.659
Potential of Cell Under Continuous Discharge Through a 100-Ohm Resistor, 100 F, volt							
Elapsed Time	0.713	0.728	0.714	0.702	0.724	0.715	0.659
0 minute	0.58	0.60	0.58	0.59	0.56	0.59	0.52
1 minute	0.45	0.51	0.50	0.47	0.46	0.47	0.44
13 minutes	0.41	0.48	0.48	0.43	0.43	0.49	0.43
25 minutes	0.40	0.47	0.47	0.41	0.41	0.49	0.42
37 minutes	0.39	0.46	0.46	0.40	0.40	0.48	0.41
49 minutes	0.38	0.45	0.46	0.39	0.38	0.48	0.40
61 minutes	0.37	0.42	0.44	0.37	0.34	0.48	0.37
2 hours	0.33	0.37	0.43	0.33	0.29	0.46	0.32
4 hours	0.29	0.35	0.43	0.32	0.25	0.42	0.28
6 hours	0.25	0.30	0.36	0.36	0.20	0.40	0.26
12 hours	0.23	0.28	0.35	0.33	0.19	0.39	0.22
18 hours	0.22	0.25	0.34	0.29	0.18	0.38	0.18
24 hours	0.21	0.23	0.35	0.27	0.14	0.38	0.13
36 hours	0.19	0.22	0.34	0.25	0.12	0.37	0.11
48 hours	0.17	0.23	0.32	0.22	0.10	0.35	0.10
57 hours							

A-1

TABLE A-1. (Continued)

Elapsed Time	Cell Voltages During Recovery After Removing Load, volt						
10 seconds	0.21	0.27	0.375	0.252	0.108	0.445	0.133
10 minutes	0.452	0.534	0.524	0.493	0.249	0.539	0.28
20 minutes	0.542	0.583	0.540	0.562	0.333	0.553	0.37
21 hours	0.61	0.61	0.64	0.665	0.615	0.69	0.61
67 hours	0.62	0.63	0.685	0.655	0.623	0.693	0.615

(1) These voltages were read after all the cells were assembled but before they were heated to 100 F.

(2) These voltages were read 18 hours after cell assembly. The continuous-discharge test followed immediately thereafter.

TABLE A-2. OPEN-CIRCUIT VOLTAGE AND POTENTIAL UNDER CONTINUOUS DISCHARGE FOR FERROBORON CELLS IN ACID ELECTROLYTE(1)

Ferroboron Lot No. Cell No.:	382			383			403		
	19A1	19A2	19A3	19B1	19B2	19B3	19C1	19C2	19C3
Open-Circuit Voltage, volt:(2)	0.547	0.563	0.537	0.565	0.558	0.581	0.554	0.556	0.541
Open-Circuit Voltage, volt:(3)	0.355	0.553	0.495	0.400	0.270	0.369	0.352	0.370	0.471

Elapsed Time	Potential of Cell Under Continuous Discharge Through a 100-Ohm Resistor, 100 F, volt									
	0.26	0.50	0.38	0.29	0.13	0.27	0.25	0.29	0.42	
1 minute	0.21	0.43	0.30	0.25	0.11	0.25	0.18	0.24	0.33	
13 minutes	0.22	0.40	0.30	0.24	0.14	0.26	0.18	0.23	0.33	
25 minutes	0.22	0.38	0.27	0.24	0.16	0.25	0.20	0.23	0.27	
37 minutes	0.18	0.37	0.34	0.23	0.22	0.26	0.22	0.23	0.25	
49 minutes	0.24	0.36	0.33	0.23	0.23	0.26	0.23	0.23	0.27	
1 hour	0.20	0.35	0.32	0.23	0.23	0.25	0.24	0.24	0.25	
1.5 hours	0.18	0.33	0.32	0.23	0.13	0.24	0.23	0.24	0.24	
2 hours	0.18	0.28	0.27	0.22	0.11	0.24	0.18	0.22	0.23	
3 hours	--	--	--	--	0.16	--	--	--	--	
3.5 hours	--	--	--	--	0.18	--	--	--	--	
3.75 hours	0.18	0.28	0.21	0.21	0.13	0.22	0.16	0.20	0.22	
4 hours	0.18	0.27	0.18	0.20	0.09	0.21	0.15	0.20	0.21	
5 hours	0.17	0.24	0.15	0.20	0.09	0.21	0.14	0.18	0.19	
7 hours	0.15	0.23	0.14	0.19	0.09	0.19	0.12	0.17	0.19	
9 hours										

(1) Electrolyte same as for calcium boride cells.

(2) These voltages were read from the cells after they were all assembled but before they were heated to 100 F.

(3) These voltages were read from the cells approximately 18 hours after the cells were assembled. The continuous-discharge test followed immediately thereafter.

TABLE A-3. OPEN-CIRCUIT VOLTAGE AND INSTANTANEOUS VOLTAGE UNDER VARYING LOADS AND POTENTIAL UNDER CONTINUOUS DISCHARGE FOR FERROBORON CELLS IN BASIC ELECTROLYTE(1)

Ferroboron Lot No.:	382			403			383		
	23A1	23A2	23A3	23B1	23B2	23B3	23C1	23C2	23C3
Cell No.:									
Open-Circuit Voltage, volt:	0.551	0.693	0.522	0.449	0.434	0.453	0.492	0.497	0.505
Load, ohms	Instantaneous Voltage Under Load, volt								
100,000	--	0.690	--	--	0.425	--	--	0.495	--
50,000	--	0.688	--	--	0.425	--	--	0.495	--
10,000	--	0.689	--	--	0.426	--	--	0.495	--
5,000	--	0.688	--	--	0.425	--	--	0.495	--
1,000	--	0.687	--	--	0.423	--	--	0.492	--
500	--	0.683	--	--	0.422	--	--	0.491	--
250	--	0.680	--	--	0.418	--	--	0.488	--
100	0.532	0.673	0.493	0.422	0.408	0.425	0.473	0.481	0.500

Potential Under Continuous Discharge for Ferroboron Cells, 100-Ohm Load, at 100 F, volt									
Elapsed Time(2)	0.07	0.04	0.05	-0.16	0.00	-0.14	0.47	-0.11	0.06
1 minute	--	--	--	--	--	--	0.46	--	--
13 minutes	--	--	--	--	--	--	0.44	--	--
25 minutes	--	--	--	--	--	--	0.15	--	--
37 minutes	--	--	--	--	--	--	0.00	--	--
49 minutes	--	--	--	--	--	--	0.00	--	--
1 hour	--	--	--	--	--	--	-0.10	--	--
2 hours	--	--	--	--	--	--	-0.11	-0.09	0.03
3 hours, 20 minutes	0.04	0.03	0.03	-0.13	-0.10	-0.12			

(1) 31 per cent potassium hydroxide electrolyte.

(2) The continuous-discharge test was conducted approximately 18 hours after the open-circuit measurements were made.

TABLE A-4. OPEN-CIRCUIT VOLTAGE AND INSTANTANEOUS VOLTAGE UNDER VARYING LOADS AND POTENTIAL UNDER CONTINUOUS DISCHARGE FOR FERROBORON CELLS IN BASIC ELECTROLYTE<sup>(1)</sup>

Ferroboron Lot No.:	382		383		403	
	25A1	25A2	25B1	25B2	25C1	25C2
Cell No.:						
Open-Circuit Voltage, volt:	0.498	0.494	0.481	0.467	0.412	0.408
Load, ohms	Instantaneous Voltage Under Load, volt					
1,000	0.494	0.493	0.480	0.465	0.412	0.408
500	0.492	0.492	0.480	0.463	0.411	0.406
250	0.488	0.489	0.478	0.462	0.409	0.403
100	0.480	0.483	0.470	0.452	0.403	0.398
50	0.472	0.462	0.467	0.441	0.398	0.388
Potential Under Continuous Discharge for Ferroboron Cells, 100-Ohm Load, at 100 F, volt						
Elapsed Time <sup>(2)</sup>						
1 minute	-0.09	0.35	-0.13	0.00	-0.17	0.00
13 minutes	--	0.38	--	--	--	--
25 minutes	--	0.38	--	--	--	--
37 minutes	--	0.37	--	--	--	--
49 minutes	--	0.02	--	--	--	--
1 hour	-0.08	0.02	-0.11	0.02	-0.16	0.00
2.5 hours	-0.08	0.02	-0.10	0.02	-0.16	0.00

(1) Electrolyte in 35 per cent KOH, 5 per cent ZnO.

(2) The continuous-discharge test was conducted approximately 18 hours after the open-circuit measurements were made.